

## Rapidly Functionalized, Water-Dispersed Carbon Nanotubes at High Concentration

Yubing Wang, Zafar Iqbal,\* and Somenath Mitra\*

*Contribution from the Department of Chemistry and Environmental Science,  
New Jersey Institute of Technology, Newark, New Jersey 07102*

Received May 8, 2005; E-mail: iqbal@njit.edu; mitra@njit.edu

**Abstract:** Microwave-assisted functionalization of single-wall carbon nanotubes (SWNTs) in a mixture of nitric and sulfuric acids was carried out to synthesize highly water-dispersible nanotubes. Stable concentrations as high as 10 mg/mL were obtained in deionized water that are nearly 2 orders of magnitude higher than those previously reported. This was after only 3 min of functionalization reaction. Fourier transform infrared spectra showed the presence of carboxylated ( $-\text{COOH}$ ) and acid sulfonated ( $-\text{SO}_2\text{OH}$  or  $-\text{SO}_3^- \text{H}^+$ ) groups on the SWNTs. On the basis of elemental analysis, it was estimated that one out of three carbon atoms was carboxylated, while one out of 10 carbon atoms was sulfonated. The Raman spectra taken both in aqueous dispersion and in the solid phase indicated charge transfer from the SWNT backbone to the functional groups. Scanning electron microscope images of thin films deposited from an aqueous suspension showed that the SWNTs were aligned parallel to one another on the substrate. The images also indicated some reduction in average length of the nanotubes. Transmission electron microscope images of thin films from a dilute methanol dispersion showed that the SWNTs were extensively debundled. Laser light scattering particle size measurements did not show evidence for the existence of particles in the 3–800 nm size range, indicating that the functionalized SWNTs might have dispersed to have formed a true solution. Moreover, the microwave-processed SWNTs were found to contain significantly smaller amounts of the original iron catalyst relative to that present in the starting nanotubes. The electrical conductivity of a thermally annealed thin membrane obtained from the microwave-functionalized SWNTs was found to be the same as that of a similar membrane obtained from a suspension of the starting nanotubes.

### Introduction

Dispersion of single-wall carbon nanotubes (SWNTs) in water to form a stable suspension where no precipitation occurs on prolonged standing would allow a wide range of chemical derivatization and manipulation to be readily carried out. Considerable efforts have therefore been made<sup>1–12</sup> to make carbon nanotubes stably dispersed or soluble in water and in organic solvents, but to date the solubilities observed have been

relatively low; typical values at room temperature range from 0.06 to 0.08 mg of SWNT/mL of solvent.<sup>1</sup> Different strategies have been employed to achieve dispersion; one of the first was to shorten the SWNTs down to about 100–300 nm by prolonged and vigorous acid treatment.<sup>2</sup> Dispersion of full-length nanotubes has mostly been achieved by noncovalent wrapping of water-soluble macromolecules on the nanotubes.<sup>3–5</sup>

Much of the effort aimed at SWNT functionalization has involved the use of conventional chemical techniques, such as refluxing and sonication. Many of these reactions were required to be carried out over long periods of time. For example, for carboxylation, the reaction mixture was typically refluxed in concentrated  $\text{HNO}_3$  for 10–50 h. Further functionalization, such as diimide-activated amidation<sup>11</sup> and 1,3-dipolar cycloaddition,<sup>8</sup> may require additional days of reaction time. The functionalization of carbon nanotubes by conventional chemical processing is therefore a tedious and time-consuming process. Consequently, there is an urgent need to develop techniques for rapid chemical functionalization of SWNTs.

Chemistry under microwave radiation is known to be somewhat different, faster and more efficient,<sup>13,14</sup> than under

- (1) Pompeo, F.; Resasco, D. E. *Nano Lett.* **2002**, *2*, 369.
- (2) Chen, J.; Hamon, M. A.; Hu, H.; Chen, Y.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. *Science* **1998**, *282*, 95.
- (3) Mickelson, E. T.; Chiang, I. W.; Zimmerman, J. L.; Boul, P. J.; Lozano, J.; Liu, J.; Smalley, R. E.; Hauge, R. H.; Margrave, J. L. *J. Phys. Chem. B* **1999**, *103*, 4318.
- (4) Chen, J.; Rao, A. M.; Lyuksyutov, S.; Itkis, M. E.; Hamon, M. A.; Hu, H.; Cohn, R. W.; Eklund, P. C.; Colbert, D. T.; Smalley, R. E.; Haddon, R. C. *J. Phys. Chem. B* **2001**, *105*, 2525.
- (5) O'Connell, M. J.; Boul, P.; Ericson, L. M.; Huffman, C.; Wang, Y.; Haroz, E.; Kuper, C.; Tour, J.; Ausman, K. D.; Smalley, R. E. *Chem. Phys. Lett.* **2001**, *342*, 265.
- (6) Lin, Y.; Allard, L. F.; Sun, Y.-P. *J. Phys. Chem. B* **2004**, *108*, 3760.
- (7) Qin, S.; Qin, D.; Ford, W. T.; Resasco, D. E.; Herrera, J. E. *Macromolecules* **2004**, *37*, 752.
- (8) Georgakilas, V.; Kordatos, K.; Prato, M.; Guldi, D. M.; Holzinger, M.; Hirsch, A. *J. Am. Chem. Soc.* **2002**, *124*, 760.
- (9) Feng, L.; Li, H.; Li, F.; Shi, Z.; Gu, Z. *Carbon* **2003**, *41*, 2385.
- (10) Peng, H.; Alemany, L. B.; Margrave, J. L.; Khabashesku, V. N. *J. Am. Chem. Soc.* **2003**, *125*, 15174.
- (11) Huang, W.; Taylor, S.; Fu, K.; Lin, Y.; Zhang, D.; Hanks, T. W.; Rao, A. M.; Sun, Y.-P. *Nano Lett.* **2002**, *2*, 311.
- (12) Matsuura, K.; Hayashi, K.; Kimizuka, N. *Chem. Lett.* **2003**, *32*, 212.

- (13) Bensebaa, F.; Zavaliche, F.; L'Ecuyer, P.; Cochrane, R. W.; Veres, T. *J. Colloid Interface Sci.* **2004**, *277*, 104.
- (14) Zhou, G.; Pol, V. G.; Palchik, O.; Kerner, R.; Sominski, E.; Koltypin, Y.; Gedanken, A. *J. Solid State Chem.* **2004**, *177*, 361.

conventional chemical processing conditions. Microwave processing also reduces the need for solvents; thus it is eco-friendly. It has been exploited in a variety of organic syntheses and reactions, where high yields, rapid reaction under controlled temperature and pressure, and high-purity products due to the short residence times have been reported.<sup>15,16</sup> Additionally, the chemical activation parameters are modified due to further polarization of the dipoles under microwave radiation.<sup>17</sup>

In this paper we report a rapid and environmentally friendly, microwave-induced method<sup>18</sup> to prepare highly water-dispersible single-walled carbon nanotubes (SWNTs) in about 3 min. Characterization of the functionalized SWNTs in aqueous suspension has been carried out by Raman and near-IR spectroscopy and light scattering. Raman and Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), and electron microscopy are used to characterize the functionalized SWNTs precipitated from solution. Electrical conductivity measurements of a membrane of functionalized SWNTs showed 33% reduction compared to the starting material, but the starting conductivity was fully recovered after high-temperature annealing under Ar.

## Experimental Section

The starting SWNTs, which were prepared by the high-pressure carbon monoxide (HiPCO) chemical vapor deposition process,<sup>19,20</sup> were obtained from Carbon Nanotechnologies Inc. All other chemicals were purchased from Sigma—Aldrich. The starting SWNTs were not soluble (or dispersible) in deionized (DI) water or alcohol even after prolonged sonication. Suspensions were formed where the SWNTs quickly agglomerated and settled down to the bottom of the container.

The experiments resulting in functionalization and stable dispersion were carried out in a CEM Model 205 microwave oven with a 100 mL closed-vessel reaction chamber lined with Teflon PFA and connected to a 0–200 psi pressure control system. The microwave system could be programmed to operate at different pressures, power levels, and time periods. Up to 200 psi of pressure and 900 W of power could be applied for a reaction. For safety reasons, the microwave oven was placed in a fume hood.

In a typical reaction, 10–20 mg of as-received, pure SWNTs were added to 20 mL of a 1:1 mixture of 70% nitric acid and 97% sulfuric acid aqueous solutions in the reaction chamber. (The acid mixture is highly corrosive. Extreme care should therefore be exercised during handling.) The microwave power was set at 50% of a total of 900 W, and the pressure was set at 20 psi. The reaction vessel was then subjected to microwave radiation for 1, 2, 3, 5, 10, and 20 min. Functionalization of the SWNTs as determined by FTIR spectroscopy and the dispersion of SWNTs was not observed when the SWNT–acid mixture was not subjected to microwave radiation. Three minutes of microwave irradiation was found to be the optimum time for the reaction. At this reaction time, a large fraction of the SWNTs dispersed in the acid mixture with minimal loss of nanotubes due to microwave-induced oxidation. The mixture was then diluted with DI water and filtered through 10  $\mu$ m poly(tetrafluoroethylene) (PTFE) filter paper, and the filtrate was transferred to a dialysis bag with nominal molecular weight cutoff of 12 000–14 000. The bag was placed in a beaker containing DI water. The DI water was continually replaced till the



**Figure 1.** Photographs of SWNT dispersions of various concentrations in deionized water: (A) 0.05, (B) 0.1, (C) 0.2, (D) 0.3, (E) 0.5, and (F) 2 mg/mL.

pH of the filtrate in the bag reached 7. The filtrate was then removed and concentrated in a vacuum evaporator. The functionalized solid SWNT residue obtained from the evaporator was dried overnight at room temperature in a vacuum and used for quantitative solubility testing and for the characterization measurements discussed below.

Field emission scanning electron microscope (SEM) images were taken using a LEO 1530 electron microscope, and transmission electron microscope (TEM) images were recorded using a Topcon 200 kV ultra-high-resolution microscope. The SEM images were obtained on microwaved SWNTs deposited on a conducting silicon wafer from a concentrated aqueous solution of the nanotubes, while the TEM images were obtained on thin films deposited on TEM grids from a dilute methanol solution of the microwaved SWNTs. The infrared and Raman spectra were recorded using a Perkin-Elmer FTIR spectrometer and a Horiba/Jovin Yvon Lab Ram system with 632.8 nm excitation, respectively. FTIR measurements were made on thin films deposited from a methanol solution of SWNTs on a single-crystal sodium chloride plate. The Raman spectra were measured on aqueous solutions of the microwaved SWNTs and on the functionalized SWNT solids. The thermogravimetric analyses (TGA) were performed with a Universal V3.7A instrument on pristine and microwave-functionalized SWNTs. Laser light-scattering particle size measurements on aqueous solutions of microwave-functionalized SWNTs were performed with a Beckman Coulter N4 Plus submicrometer particle size analyzer, which has an effective detection range from 3 to 800 nm. Sheet electrical conductivities along SWNT membrane surfaces, which all had an area of  $2.54 \times 2.54$  cm<sup>2</sup>, were measured. The free-standing SWNT membranes were self-assembled, washed, dried, and removed after slow vacuum filtration through the PTFE filter paper. Two silver pads deposited on the membrane were used as the electrical contacts. The average membrane thicknesses were measured with a micrometer.

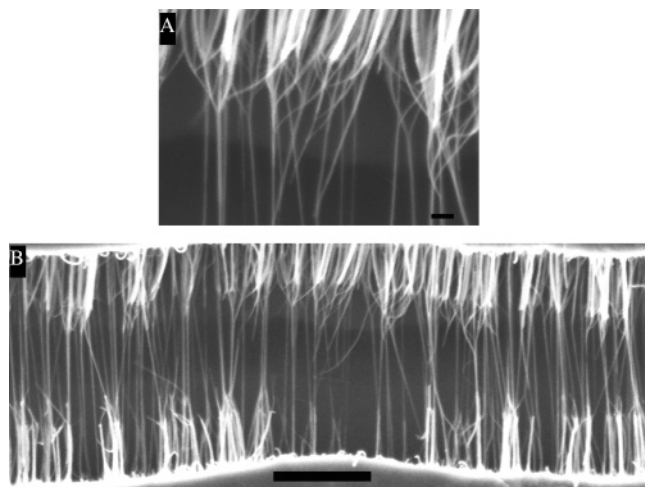
## Results and Discussion

The acid-functionalized SWNTs obtained after microwave treatment were highly dispersible in DI water and ethanol under ambient conditions. Dispersed concentration of 10 and 2.5 mg/mL were obtained in water and anhydrous alcohol, respectively. Significantly higher concentration up to 20 mg/mL was obtained in acidified water. The dispersions showed no indication of SWNT precipitation after prolonged standing (months) under ambient conditions. Photographs of typical aqueous dispersions of different concentrations of the microwave-functionalized SWNTs are shown in Figure 1.

Laser light-scattering particle size measurements at detection angles of 62.2° and 90° of the aqueous dispersions of microwave-functionalized SWNTs were compared with measurements made on an aqueous suspension of pristine SWNTs. The suspension prepared by sonication of 0.01 wt % SWNTs (0.1 mg/mL) and 0.5 wt % surfactant Triton X-100 showed particle sizes ranging from 100 to 600 nm with a maximum at 300 nm. In contrast,

- (15) Shaabani, A.; Bazgir, A. *Tetrahedron Lett.* **2004**, 45, 2575.
- (16) Ardon, M.; Hogarth, G.; Ocroft, D. T. W. *J. Organomet. Chem.* **2004**, 689, 2429.
- (17) Lewis, D. A.; Summers, J. D.; Ward, T. C.; McGrath, J. E. *J. Polym. Sci. A* **1992**, 30, 1647.
- (18) Wang, Y.; Iqbal, Z.; Mitra, S. *Carbon* **2005**, 43, 1015.
- (19) Nikolaev, P.; Bronikowski, M. J.; Bradley, R. K.; Rohmund, E.; Colbert, D. T.; Smith, K. A.; Smalley, R. E. *Chem. Phys. Lett.* **1999**, 313, 91.
- (20) Bronikowski, M. J.; Willis, P. A.; Colbert, D. T.; Smith, K. A.; Smalley, R. E. *J. Vac. Sci. Technol.* **2001**, A19, 1800.





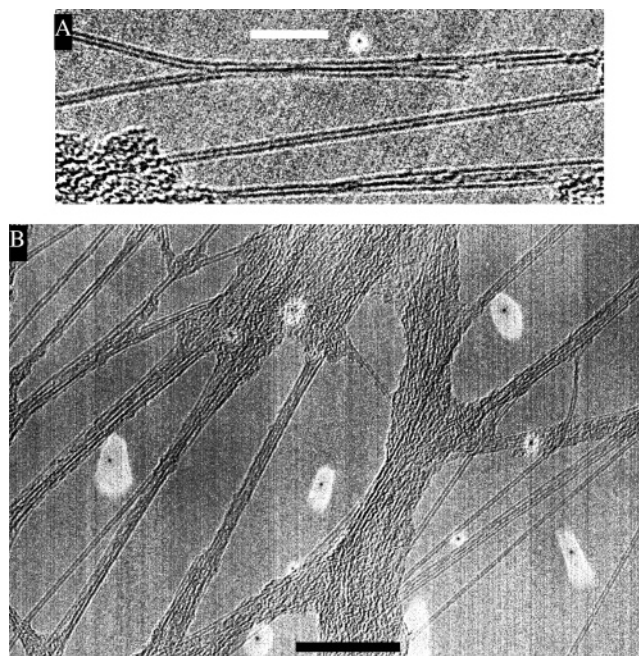
**Figure 2.** SEM images of microwave-functionalized SWNTs. (A) Higher magnification SEM image showing alignment of the SWNTs deposited from aqueous solution discussed in the text; scale bar = 50 nm. (B) Lower magnification SEM image of the aligned SWNTs; scale bar = 500 nm.

a 0.5 mg/mL aqueous dispersion of microwave-functionalized SWNTs (Figure 1E) did not show any evidence of the existence of particles in the 3–800 nm size range at the same detection angles, indicating that the functionalized SWNTs might have dispersed to have formed a true solution.

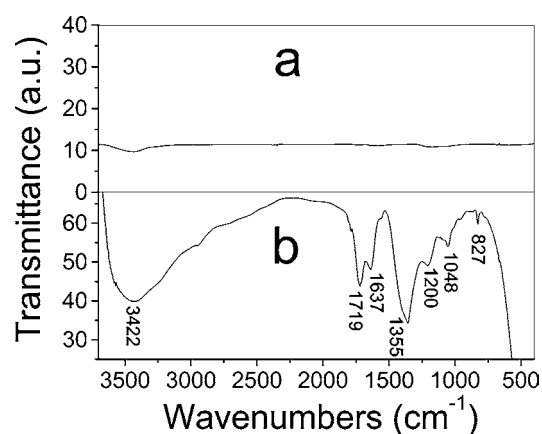
SEM images of the microwave functionalized SWNT bundles are shown in Figure 2. On the basis of the TEM results (see below) obtained from more dilute dispersions in methanol, it is evident that the bundles are weakly held together since the images show large numbers of individual tubes and thin bundles. The functionalized SWNTs for SEM imaging were deposited as a thin film from a drop of aqueous dispersion on a silicon wafer. The images show that the deposited bundles were aligned parallel to one another along the substrate, probably due to hydrophobic forces and nanotube–nanotube interactions. This alignment was observed each time after the evaporation of a drop of SWNT dispersion. The average length of the aligned SWNTs was around 1  $\mu\text{m}$  (Figure 2B). This might indicate a reduction in length of SWNTs as a result of the microwave treatment. Lowering the acid concentration, reaction pressure, and microwave power may minimize this length reduction.

A typical high-resolution TEM image from microwave-functionalized SWNTs in Figure 3A showed individual and thin SWNT bundles with uneven, disordered sidewalls due to extensive side-group functionalization. The lower magnification TEM in Figure 3B showed that most SWNTs were debundled into individual tubes or very thin bundles. The individual tubes in the bundles deposited from concentrated aqueous solution observed in the SEM images (Figure 2) were probably exfoliated in the dilute methanol solution used for TEM sample preparation to form mostly individual nanotubes or thin bundles.

FTIR spectra of the microwave-functionalized SWNTs were obtained to determine the structure of the chemical groups formed on the nanotube sidewalls and tube ends. Like graphite, the FTIR spectrum of the pristine nanotubes (Figure 4a) is practically featureless with extremely low infrared absorption intensities. After the microwave-induced functionalization, a typical FTIR spectrum (Figure 4b) showed a number of infrared lines, which were assigned as follows:<sup>21</sup> The line at 1719  $\text{cm}^{-1}$  was assigned to the C=O stretching mode of the -COOH groups



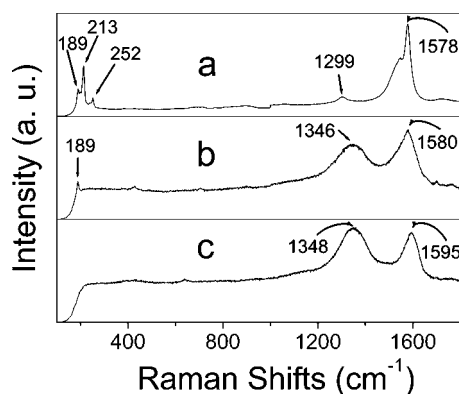
**Figure 3.** TEM images of microwave-functionalized SWNTs on a holey carbon covered grid. (A) Typical high-resolution TEM image of microwave functionalized SWNTs, scale bar = 10 nm, showing some bundling and individual tubes. (B) TEM image of debundled and bundled SWNTs; scale bar = 20 nm.



**Figure 4.** FTIR spectra of microwave-functionalized SWNTs: (a) pristine SWNTs in KBr; (b) microwave-functionalized SWNTs from a thin film deposited from methanol dispersion on to a NaCl window.

(where the carbon is from the SWNT backbone) on the SWNTs, whereas the intense, broad line centered at 3422  $\text{cm}^{-1}$  was assigned to the -OH stretching mode of the -COOH group. The line at 1637  $\text{cm}^{-1}$  was assigned to the SWNT C=C graphitic stretching mode that is infrared-activated by extensive sidewall functionalization. The strong line observed at 1355  $\text{cm}^{-1}$  was assigned to the asymmetric SO<sub>2</sub> stretching mode of the acid sulfonate (-SO<sub>2</sub>-OH) group, whereas the lower frequency line at 1200  $\text{cm}^{-1}$  was assigned to the SO<sub>2</sub> symmetric stretching mode. The shoulder near 2600  $\text{cm}^{-1}$  was assigned to the -OH group of the sulfonic acid group. The FTIR spectrum is consistent with elemental analysis of the functionalized SWNTs, which showed that one in three of the carbon atoms on the SWNT backbone was carboxylated, and one in 10 was sul-

(21) Socrates, G. *Infrared and Raman Characteristic Frequencies: Tables and Charts*; John Wiley & Sons: New York, 2001; pp 220–222.

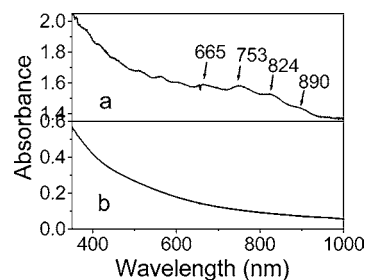


**Figure 5.** Raman spectra (excited by 632.8 nm radiation) of microwave-functionalized SWNTs: (a) pristine SWNTs, (b) microwave-functionalized SWNTs in solid phase precipitated by evaporation from an aqueous dispersion of 0.5 mg of SWNTs in 1 mL; and (c) dispersion of 2.0 mg of microwave-functionalized SWNTs/mL of DI water.

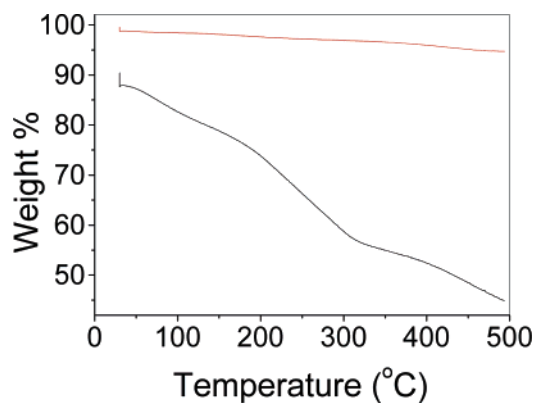
fonated. In addition, an FTIR spectrum taken in KBr (not shown here) showed a line of medium intensity at  $592\text{ cm}^{-1}$ , which was assigned to the C–S stretching mode, thus implying that the acid sulfonate functionalization was covalent. In some samples, the presence of trace water formed the hydrated sulfonic acid group,  $-\text{SO}_3^-\text{H}^+\text{H}_2\text{O}$ , which gave rise to a strong infrared line at  $1114\text{ cm}^{-1}$  assigned to the asymmetric stretching mode of  $\text{SO}_3$  and a shoulder near  $1000\text{ cm}^{-1}$  assigned to the corresponding symmetric stretching mode. The combination of extensive carboxylation and acid sulfonation on the SWNTs resulted in charge-transfer-induced formation of an SWNT polyelectrolyte salt in the presence of polar solvent molecules followed by dissolution via ionic dissociation.

As compared to the starting SWNTs of Figure 5a, the Raman spectrum (Figure 5c) of an aqueous dispersion of the microwave-functionalized SWNTs showed an upshift of the C–C tangential mode frequency at  $1595\text{ cm}^{-1}$  by about  $20\text{ cm}^{-1}$ , and also the radial breathing modes (RBMs) disappeared. These are known to be characteristic of charged SWNTs.<sup>22,23</sup> The RBM lines, however, appeared in the solid state as the SWNTs were precipitated from a dispersion by concentration (Figure 5b). A single RBM line was typically seen in the functionalized SWNTs (Figure 5b), in contrast to multiple ones in the starting SWNTs (Figure 5a). This indicated that the microwave process probably oxidized some of the chemically reactive SWNTs of smaller diameter. After the functionalization, the disorder-induced SWNT line near  $1320\text{ cm}^{-1}$  showed a significant increase in intensity both in aqueous solution and in the solid state. This is in agreement with previous observations of functionalized SWNTs.<sup>24</sup> Similarly, the resonance enhancement of the Raman spectrum observed in the starting SWNTs was significantly reduced for the functionalized SWNTs.

To characterize the electronic states of the microwave-functionalized SWNTs, visible–near-infrared (vis-NIR) absorption spectra of aqueous dispersions and a suspension of pristine SWNTs in dimethylformamide were measured. The spectra are shown in Figure 6. Interband transitions between van Hove singularities in the electronic density of states of the starting



**Figure 6.** Visible–near-infrared (vis-NIR) spectra of (a) pristine SWNTs suspended in dimethylformamide (0.05 mg/mL) and (b) aqueous dispersion of microwave-reacted SWNTs (0.5 mg/mL).



**Figure 7.** Thermogravimetric analysis (TGA) data under pure nitrogen at a heating rate of  $10\text{ }^\circ\text{C/min}$  for (top, red) pristine SWNTs and, (bottom, black) microwave-functionalized SWNTs.

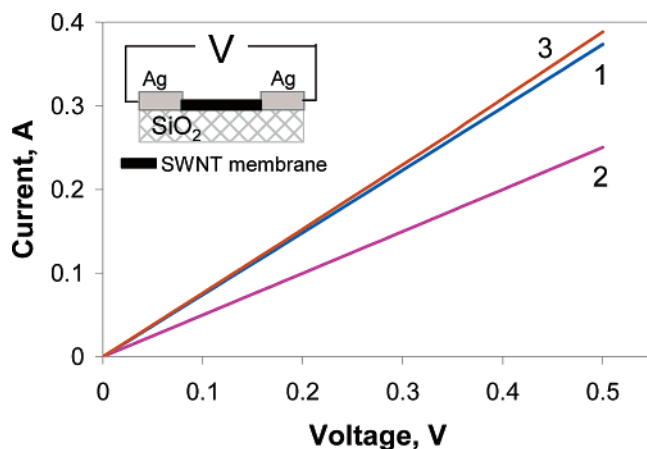
SWNTs were observed at 665, 753, 824, and 890 nm in the spectrum of the pristine SWNTs (Figure 6a). The corresponding spectrum of the aqueous dispersion of microwave-functionalized solution did not show these transitions, confirming the occurrence of microwave SWNT functionalization. This is in agreement with what has been previously reported.<sup>24</sup>

The effect of thermal treatment on the functionalized SWNTs was studied by thermogravimetric analysis (TGA) measurements and compared with pristine SWNTs. The heating was carried out under dry nitrogen at a heating rate of  $10\text{ }^\circ\text{C/min}$  from 30 to  $500\text{ }^\circ\text{C}$ . The TGA traces (shown in Figure 7) showed that the functionalized SWNTs decreased in weight by nearly 50%, most likely due to the loss of the functional groups.

The conductivity of membranes fabricated from both pristine and microwave-treated SWNTs was measured and compared. The pristine SWNT membrane was made from an aqueous SWNT suspension in a surfactant (Triton X-100). The surfactant was removed by washing with DI water and methanol, and annealing took place at  $700\text{ }^\circ\text{C}$  under argon for 1 h. The membrane made from microwave-treated SWNTs was fabricated in two steps. In the first step, 150 mg of pristine SWNTs was added to 30 mL of the acid mixture described above, and the mixture was microwaved for 3 min. The acids were removed by filtration and washing with DI water. Then, the SWNTs collected were suspended in water by sonication in a water bath in the absence of a surfactant, and a membrane was deposited by filtration through PTFE filter paper ( $0.5\text{ }\mu\text{m}$  pore size).

Part of the membrane made from microwave-treated SWNTs was also annealed at  $700\text{ }^\circ\text{C}$  under argon for 1 h. Both the annealed and unannealed microwaved SWNT membranes along with the annealed pristine SWNT membrane were used for the

- (22) Penicaud, A.; Poulin, P.; Derre, A.; Anglaret, E.; Petit, P. *J. Am. Chem. Soc.* **2005**, *127*, 8.
- (23) Bendjab, N.; Anglaret, E.; Bantignies, J. L.; Petit, P.; Mathis, C.; Lefrant, S. *Phys. Rev. B* **2001**, *64*, 245424.
- (24) Hudson, J. L.; Casavant, M. J.; Tour, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 11158.



**Figure 8.**  $I$ – $V$  characteristics of 43  $\mu\text{m}$  thick SWNT membranes, which have an area of  $0.1 \times 0.1$  square inches. (1, dark blue) Annealed pristine SWNTs; (2, purple) microwaved SWNT membrane before annealing; (3, orange) annealed, microwaved SWNT membrane.

conductivity measurements. The measurement setup is schematically shown as the inset in Figure 8.

Figure 8 shows the current–voltage ( $I$ – $V$ ) traces for the three membranes. All showed ohmic behavior. The dc conductivity of the microwaved nanotube membrane (unannealed, curve 2) is reduced by 33%, compared to the pristine SWNT membrane (curve 1). The increase in resistivity was significantly lower than that reported previously for oxidized SWNTs.<sup>25,26</sup> Most importantly, the loss in conductivity of microwaved SWNTs was fully recovered after annealing, as evident from curve 3. The calculated bulk resistivity of the annealed SWNTs membrane is about  $6 \times 10^{-3} \Omega \text{ cm}$ . This result indicated that the microwave-induced functionalization indeed reduces electrical conductivity; however, it can be recovered after high-temperature annealing.

We also observed that aqueous dispersions of microwave-functionalized SWNTs were electrically conductive with an ionic conductivity in DI water of  $215.8 \mu\text{S}$  relative to that of  $1.5 \mu\text{S}$  for pure DI water. This raises the possibility for electrical manipulation (such as electrodeposition of thin films) of the

SWNTs from a solution phase. Another interesting observation was that the microwave-functionalized SWNTs showed very low concentrations of leftover iron from the starting catalyst as determined by ferromagnetic magnetic resonance (FMR) spectroscopy, which is extremely sensitive to the presence of magnetic particles.<sup>27</sup> The starting HiPCO-prepared SWNTs showed a strong FMR signal, indicating the presence of a significant concentration of the iron catalyst. The low residual concentration may be due to small amounts of iron, which remained trapped in the interstitial sites of the thin SWNT bundles.

## Conclusions

Microwave treatment of a suspension of starting SWNTs in a 1:1 mixture of 70% nitric acid and 97% sulfuric acid in water was found to form carboxylated and acid-sulfonated SWNTs with relatively high dispersivity in DI water and ethanol. Elemental analysis indicated that one in three and one in 10 carbon atoms on the SWNT structure were carboxylated and sulfonated, respectively. Some reduction in average length of the nanotubes, sidewall disordering, and extensive debundling due to functionalization were also observed. Thermogravimetric measurements to 500  $^{\circ}\text{C}$  showed the loss of the functional groups, suggesting that structural order on the sidewalls can be restored by thermal treatment. The loss in electrical conductivity after microwave treatment can be fully recovered after high-temperature annealing in argon. The results also indicate the removal of a large fraction of the iron catalyst particles during the microwave treatment. The very high dispersivity in polar solvents will enable SWNTs to be more easily processed during chemical and biochemical reactions, physical blending, and thin film/nanocomposite formation. Moreover, their alignment during deposition as a thin film from aqueous suspension will allow the fabrication of a variety of nanoscale device architectures and aligned nanocomposite structures.

**Acknowledgment.** U.S. Environmental Protection Agency (EPA) and U.S. Army are acknowledged for financial support. We thank Frank Owens and Husnu Unalan for help with the Raman and TEM measurements.

JA053003Q

(25) Kovtyukhova, N. I.; Mallouk, T. E.; Pan, L.; Dickey, E. J. *Am. Chem. Soc.* **2003**, *125*, 9761.

(26) Kovtyukhova, N. I.; Mallouk, T. E. *J. Phys. Chem. B* **2005**, *109*, 2540.

(27) Owens, F. J.; Iqbal, Z.; Belova, L.; Rao, K. V. *Phys. Rev. B* **2004**, *69*, 033403.